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FIELD EXPERIMENTS ON TREATMENT OF FLUORINE SPILLS WITH WATER OR SODA ASH

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FIELD EXPERIMENTS ON TREATMENT OF FLUORINE SPILLS WITH WATER OR SODA ASH

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SUMMARY

An investigation was made of the use of water or soda ash as a deluge agent in reducing contamination from accidental fluorine spills. Six tests were carried out in a structure which might be typical of a building in which fluorine is used. Three of the tests were with gaseous-fluorine releases and three were with liquid-fluorine releases. For five of the tests, water was sprayed on the fluorine, and in one soda ash was released on the fluorine. Data were obtained on the amount of fluorine released, quantity of water or soda ash used, amount of fluorine contamination in the test structure at various test times, and the total quantity of fluorine captured by the deluge for each test.

In all the tests, 30 to 43 percent by weight of the released fluorine was captured by the deluge agent. When gaseous fluorine was released and sprayed with water, there were no visual indications of fast reactions and there was no test-structure damage. However, the reactions were rapid enough to result in considerable amounts of fluorine being captured within a few minutes. When liquid fluorine was spilled, there were violent reactions whether the deluge agent was present or not. The resulting structural damage caused rapid loss of fluorine, but the amounts captured in these tests were about the same as with gaseous fluorine in spite of the losses. This indicated faster reaction with water for the liquid-fluorine tests. A fine water spray was more effective in reacting with fluorine than was a coarse spray.

INTRODUCTION

Elemental fluorine is being used at many industrial and research sites throughout the country. The potential use of fluorine as an oxidant has resulted in the handling of large quantities in experimental rocket propulsion systems. Greater performance can be obtained with fluorine than with other stable oxidizers in combination with various rocket fuels.

Fluorine is a very reactive and toxic chemical, therefore special precautions must be taken in using it. Recommended materials of construction and handling techniques are reported in references 1 to 4. Methods are also known for intentionally disposing of fluorine in a controllable, safe manner (refs. 5 to 8). However, an unintentional escape of fluorine from a system (e.g., leaks, burnouts, malfunctions of equipment, etc.) can damage equipment and create a dangerous toxic atmosphere. Information is not available on means of treating such accidental fluorine spills to reduce contamination. This report describes experiments in which liquid- and gaseous-fluorine releases were deluged with either water or soda ash in a field test structure. The purpose was to determine if the reactions would result in significant capture of fluorine by the deluge agent under conditions which may exist in a normal structure that does not completely confine the products or resist explosive reaction.

Water was selected as one inerting agent because of its ease of application and storage. Although the reaction of fluorine and water forms hydrofluoric acid (ref. 9), the acid can be diluted with excess water, collected in a treatment tank, and neutralized with caustic.

Soda ash powder was selected as a second inerting agent because it directly forms a relatively inert and stable compound with fluorine (sodium fluoride). Unpublished results (General Chemical Co.) have indicated that fluorine contamination downwind of a spill can be reduced by chemical powders; however, determination of the amount of fluorine reacted with the powders was not made for these tests. Soda ash systems would undoubtedly be more complicated than a water deluge system, but appear practical; dry-chemical fire extinguishing systems use a similar powder.

The results from this investigation show the total fluorine captured, amount remaining unreacted in the test structure, and the amount which leaked out of the structure. Variations in fluorine concentration with time and data on fluorine contamination around the test structure are also given.

APPARATUS

The apparatus was set up to simulate conditions as they might exist if fluorine were to escape from a flow system in a building. The test structure described as follows was not gastight and was not strong enough to resist large pressure pulses, but it did keep the gases from blowing away.

Test Structure

The 6- by 6- by 6-foot test structure (fig. 1(a)) was constructed of angle iron covered with 1/4-inch-thick asbestos board with a door and a Lucite window located in one wall. The floor of the structure was a 1-foot-deep steel pan designed to hold all the deluge agent released.

Fluorine System

Gaseous fluorine (98 to 99 percent pure) was obtained for these tests in 6-pound-capacity commercial cylinders. The cylinders were connected to a coil of stainless-steel tubing which was in an insulated drum (fig. 1(b)). The outlet of the coil of tubing went to a remotely controlled fire valve and then through the test-structure wall. The end of the tube pointed downward in the center of the structure. The fluorine cylinders were equipped with a hand valve; between this valve and the coil of tubing was a tee for helium purge and pressurization of the line when liquid fluorine was used.

Water Deluge System

City water was piped to the test structure through a flowmeter and a remotely controlled valve (fig. 1(b)). The pipe was then branched. One pipe passed through the test-structure wall to the center of the ceiling, and either a wide-angle conical spray nozzle or a multihead fog jet nozzle was mounted on it. The other pipe contained a flowmeter and hand valve and led to a ring manifold mounted on the ceiling. Four sheet-type spray nozzles were located on the ring manifold, with the sheet pattern parallel to the adjoining wall.

Soda Ash Deluge System

Powdered sodium carbonate was loaded into kraft paper troughs tacked in parallel to evenly spaced boards mounted on the test-structure ceiling. Embedded in the soda ash were rip wires doubled back under the troughs through holes in one wall to an operator a safe distance away.

Test-Structure Atmospheric Sampling System

Gas samples were collected in 5-gallon evacuated bottles connected to a stainless-steel manifold which extended diagonally through the center of the test structure (fig. 1(b)). A chemical trap and vacuum pump were also connected in series to the manifold. Solenoid valves at each sample bottle and a hand valve between the chemical trap and manifold controlled the evacuation and remote sampling procedure. The sample bottles were charged with an absorbent solution of potassium iodide and potassium hydroxide capable of reacting with all the fluorine or hydrofluoric acid in 5 gallons of atmosphere.

INSTRUMENTATION

The only instrumentation in the fluorine spill system was a pressure gage connected to the flow line. It indicated fluorine gas pressure or helium pressure when liquid fluorine was used. The accuracy of the gage was ± 2 pounds per square inch. The fluorine flow rate was not measured, but a designed restriction in the flow line kept the rate below 1/4 pound per second. For the first two tests, the amount of fluorine released was estimated from the cylinder gas pressure. For the other four tests, each cylinder was weighed to the nearest ounce before and after each test.

The water deluge flow rate was measured using a calibrated orifice in the flow line. The orifice pressure drop was shown on a differential pressure gage within ± 2 inches of water pressure. The total pressure of the water upstream of the deluge nozzles was indicated on gages which were accurate to $\pm 1/2$ pound per square inch.

Instrumentation of the test structure consisted of pressure and temperature indicators. The pressure gage was accurate to $\pm 1/2$ inch of water pressure. The interior temperature was measured with a mercury bulb-cable-gage thermometer which could indicate temperatures between 70° and 150° within 1° F.

All the previously mentioned gages, plus vacuum gages from the gas sampling bottles and a timer, were mounted on a panel close to the test structure (see fig. 1(a)). These readings were recorded by taking motion pictures of the panel.

PROCEDURE

Prior to each test, the fluorine spill system was cleaned, pressure-checked, and passivated with low-pressure fluorine gas. Further work was then halted until the wind was blowing in a direction such that any escaping fumes would not endanger personnel. The fluorine cylinder was then connected into the system, and the gas sampling bottles were evacuated.

Just before each test, moist potassium iodide test papers were set out in a grid pattern downwind of the test structure. The hand valve on the fluorine cylinder was then opened. If liquid fluorine was to be released, liquid nitrogen was put into the bath around the coiled tubing and the gaseous fluorine condensed in the tubing. When the fire valve was opened remotely, the fluorine was pushed into the test structure by a helium pressure of 50 pounds per square inch gage. If gaseous fluorine was to be released, the liquid-nitrogen bath was not used and the gaseous fluorine entered the test structure under its own pressure.

The water deluge was either turned on as soon as the fluorine fire valve was opened or after all the fluorine was in the test structure. For the first four tests, the water was sprayed from the single wide-angle conical spray nozzle in the center of the ceiling (15 percent of the total flow) and from the four sheet-type spray nozzles (85 percent of the total flow). For the fifth test, the center spray nozzle was replaced with a multihead fog-type nozzle and the flat sheet sprays were not used.

At predetermined intervals, the water was shut off, the structural atmospheric sampling line was purged, and a gas sample was sucked into an evacuated sample bottle. The water was then turned back on. While the test was going on, motion pictures were taken of both the instrument panel and test structure.

For the soda ash deluge test, an operator was positioned upwind of the test structure at the end of the rip wires from each soda ash tray. As soon as the liquid fluorine was released, he pulled the wires, which released a shower of powdered soda ash. It took about 10 seconds to release the 40 pounds of soda ash.

At the conclusion of each test, the downwind test papers were gathered and a sample of the deluge agent was removed from the test-structure floor pan. These plus the test-structure atmospheric samples were then taken to the chemical laboratory for analysis. Each sample was analyzed for total fluoride ion and for oxidizing compounds (ref. 10). The estimated accuracy of this analysis is about ±2 percent.

RESULTS AND DISCUSSION

Description of Tests

Data for the six tests are summarized in table I. The tests in which gaseous fluorine was released proceeded with little outward signs of reaction (tests 1, 2, and 3). There was no pressure increase in the test structure when the fluorine was released or when it was sprayed with water. No visible flashes were seen inside the structure. During each of the tests, the atmospheric temperature in the structure rose slowly about 15° F. The only visible sign of reaction was the escape of vapor from cracks in the structure.

The tests proceeded quite differently when liquid fluorine was released. An initial pressure surge blew out sections of the test-structure wall. Accompanying this were bright flashes and a sudden rise in the interior temperature. These indications of rapid reaction occurred when the release of fluorine and deluge agent was simultaneous (tests 4 and 6) and also when the liquid fluorine was released without deluge agent present (test 5). For test 5, the deluge water was not released until 20 seconds after the fluorine, and in the interim the pressure surge, flashes, and temperature rise occurred. The sudden vaporization of liquid fluorine could account for the pressure surge rupturing the test-structure walls but does not explain the flashes and temperature rise. Visual inspection of the structure did not show what material may have been reacting with the fluorine.

Amounts of Fluorine Captured

Results on the amounts of fluorine captured are summarized by the bar graph of figure 2. The graph shows fluorine captured, fluorine remaining in the test structure, and fluorine lost to the atmosphere by the end of each test. For each of the tests, 30 to 43 percent of the released fluorine was captured in the deluge agent.

For the first three tests with gaseous fluorine and water deluge, the amount of fluorine captured was from 34 to 43 percent of the amount released. The only variable for these tests was the length of time the water sprays were left on, which varied the amount of water used (see table I). The approximate time was 5 minutes for test 1, 7 minutes for test 3, and 10 minutes for test 2. The quantity of fluorine captured increased with the deluge time. This result would be expected because, for the tests with gaseous fluorine, the loss of fluorine to the atmosphere was not rapid, and considerable fluorine remained in the structure to be reacted with the water.

For tests 4 and 5 with liquid fluorine and water deluge, the amounts captured were 30 and 43 percent, respectively. The application of water spray was different for the two tests. For test 4, nozzles producing coarse sprays were used, while, for test 5, a single fine spray nozzle was used with one-half the water flow rate of test 4. In addition, the procedure for the two tests was different. The fluorine and water were released at the same time for test 4, while the water was not released until 20 seconds after the fluorine for test 5. In both tests, sections of the test structure were blown out as soon as the fluorine was released; therefore, fluorine was escaping from the structure prior to contact with the water for test 5. The fine water spray used for test 5 apparently increased the amount of fluorine capture despite the lower flow rate of water and the escape of fluorine prior to water deluge.

The amount of fluorine captured when powdered soda ash was dumped on liquid fluorine was 33 percent, which was of the same order as with water. Sections of the test structure were blown out by a pressure surge when fluorine and soda ash were released, as was the case for other tests with liquid fluorine. The amount of fluorine captured might have been higher if the pressure surge had not blown some of the reactants out of the structure. The rate of application of the soda ash may also affect results.

Examination of results for the gaseous-fluorine - water deluge tests (table I, tests 1, 2, and 3) indicated that most of the fluorine that escaped from the test structure did so during the time of fluorine release or shortly thereafter. This is indicated because the rate of decrease of fluorine in the structure atmosphere (samples after 30 sec for each test) and the rate of increase of fluorine in the deluge water (times of 5, 7, and 10 min for the three tests) were approximately the same. These results also show that the capture rate decreases with time as would be expected because of the decrease of fluorine concentration in the structure atmosphere.

The test-structure atmosphere samples for the liquid-fluorine spill tests show that, after 1 minute of each test, very little fluorine remained in the atmosphere (table I, tests 4, 5, and 6). The deluge captured all the fluorine it could in the first minute of each test and that which was not captured escaped through the ruptured walls. The amount of fluorine captured by the water deluge was about the same for either a gaseous or liquid release, but the rate of capture was faster when liquid fluorine was released.

Reactions

The actual reactions and their rates between fluorine and water are relatively complex in nature. Various intermediate fluorine-water reaction compounds (e.g., fluorine oxides) and radical recombinations are formed before any fairly stable products are produced (refs. 11 and 12).

The results of the laboratory analysis of the water deluge samples gave the amount of fluorine captured but did not give information as to what form or state it was in. The fluorine, as far as the analysis was concerned, could have been unreacted fluorine, intermediate products, or fluorides. Another analysis of the water deluge samples determined the amount of oxidizing material present. This oxidizing material could have been unreacted fluorine, fluorine oxide (F_2O), ozone, or hydrogen peroxide (ref. 11). For the gaseous-fluorine tests the oxidizing material found was equivalent to 18 mole percent of the total fluorine found in the deluge water. For the liquid-fluorine tests the oxidizing material was equivalent to about 1 mole percent of the total fluorine captured. These results probably reflect a difference in the reactions which took place for the gaseous- and liquid-fluorine tests.

Fluorine Dispersion

The potassium iodide test papers, which were placed in a grid pattern around the test structure, gave an indication of the total amount of fluorine (or fluorides) they had been exposed to. The fluorine leakage dispersed in a fan-shaped pattern downwind of the test structure with the greatest amount of fluorine at any one radius being at the centerline of the dispersion pattern. Near the test structure the papers indicated about $1\frac{1}{2}$ milligrams of fluoride, while those papers 130 feet directly downwind indicated two-thirds that amount.

CONCLUDING REMARKS

These field tests showed that a significant amount of fluorine can be captured and fluorine contamination thereby reduced by applying a deluge agent. The amount of fluorine which would escape from a spill area can be reduced significantly even when special provisions for containment of the spill are not made. Violent reactions did not occur when water sprays contacted gaseous fluorine, but the reaction was fast enough to result in considerable fluorine capture. When liquid fluorine was spilled, there was an explosive reaction, both with and without the deluge agent being present. This can result in damage to a structure and a rapid loss of fluorine from the area, as was the case for the tests. However, under these conditions, the fluorine reacted very rapidly with the deluge agent, and the over-all result was that about the same amount of fluorine was captured as in the gaseous-fluorine tests. The tests also indicated that, under conditions of a liquid-fluorine spill, fine water spray is more effective than coarse spray.

SUMMARY OF RESULTS

An investigation was made of the use of water or soda ash as deluge agents to reduce contamination from accidental fluorine spills. Six tests were made in a structure typical of a building in which fluorine might be used. The results with both gaseous- and liquid-fluorine releases are as follows:

1. In all the tests 30 to 43 percent by weight of the released fluorine was captured by the deluge agent.

2. There were no visual indications of fast reactions when gaseous fluorine was released or when water contacted it, and there was no damage to the test structure. Reactions were rapid enough, however, to result in considerable amounts of fluorine being captured within several minutes.

3. There were violent reactions when liquid fluorine was spilled whether or not the deluge agent was present at the time of the spill. Resulting damage caused rapid loss of fluorine from the test structure, but the amounts captured in these tests were about the same as with gaseous fluorine, which indicates faster reaction with water for these tests.

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4. A fine water spray was more effective in reacting with fluorine than was a coarse spray.

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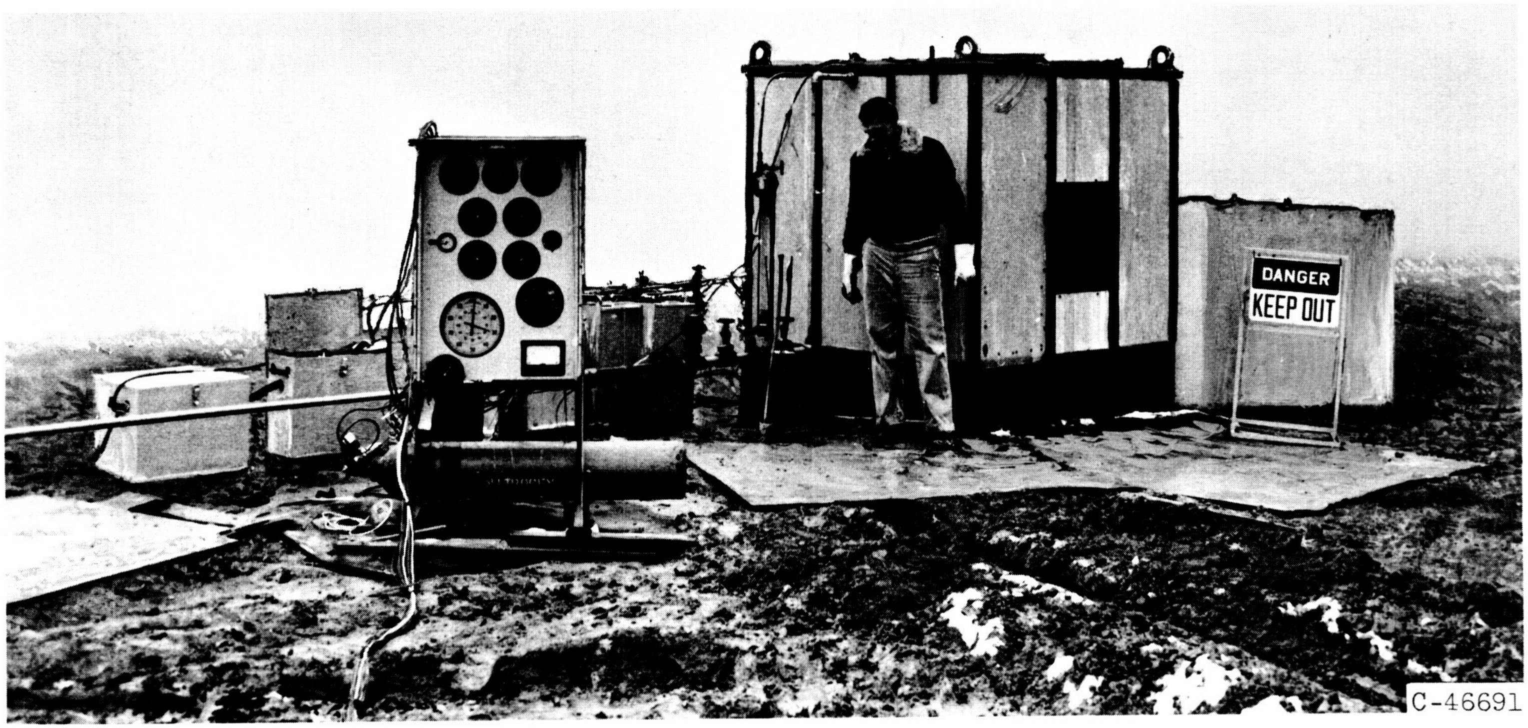
TABLE I. - SUMMARY OF DATA

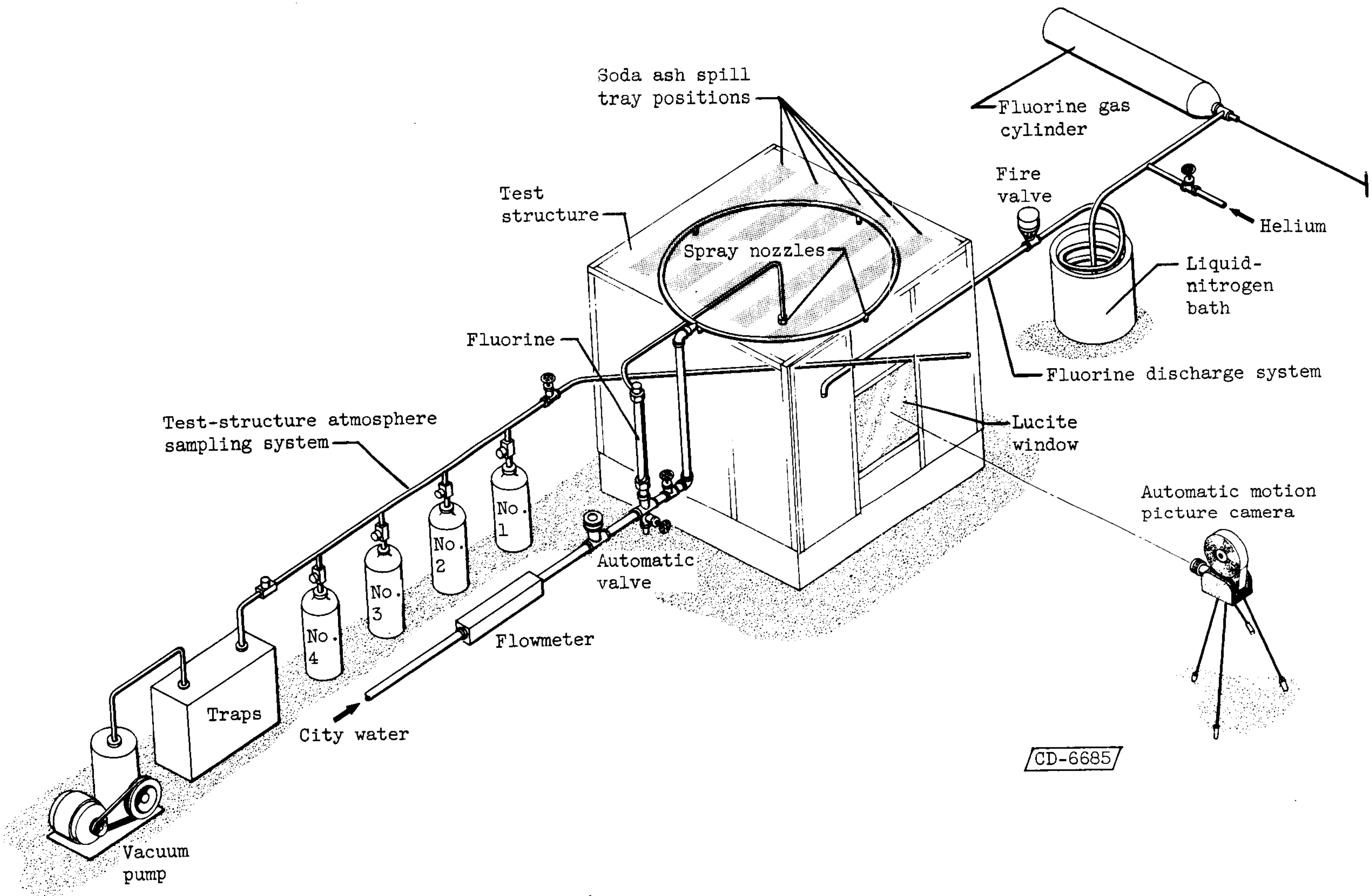
Test number	Amount of fluorine released, lb	Physical state of fluorine	Deluge agent	Approximate rate and time of water deluge		Total amount of deluge agent used	Total fluorine captured by deluge, lb	Test-structure atmosphere samples	
				Gal/min	Min			Seconds after all fluorine was released	Indicated pounds of fluorine present
1	4.95	Gas at ambient temperature	Water	15	5	78.5 Gal	1.71	30 120 300	2.47 2.51 1.68
2	5.55	Gas at ambient temperature	Water	15	10	157 Gal	2.37	30 120 300 600	2.69 2.22 1.12 1.34
3	5.25	Gas at ambient temperature	Water	15	7	102 Gal	2.03	60 120 180 360	2.05 2.10 1.67 .80
4	5.25	Liquid at -320° F	Water	15	9	135 Gal	1.59	60 180 300 480	0.086 .038 .028 .030
5	5.56	Liquid at -320° F	Water	7	[a]7	50 Gal	2.37	60 120 240 360	0.039 .077 .010 .006
6	4.94	Liquid at -320° F	Soda ash			40 Lb dumped in 10 sec	1.63	30 60 120 180	0.472 .103 .202 .140

[a]For this test there was a 20-sec delay between the release of the fluorine and the release of the deluge water; for all other tests the releases were simultaneous.



(a) Outside view.

Figure 1. - Test installation.



(b) Schematic diagram.

Figure 1. - Concluded. Test installation.

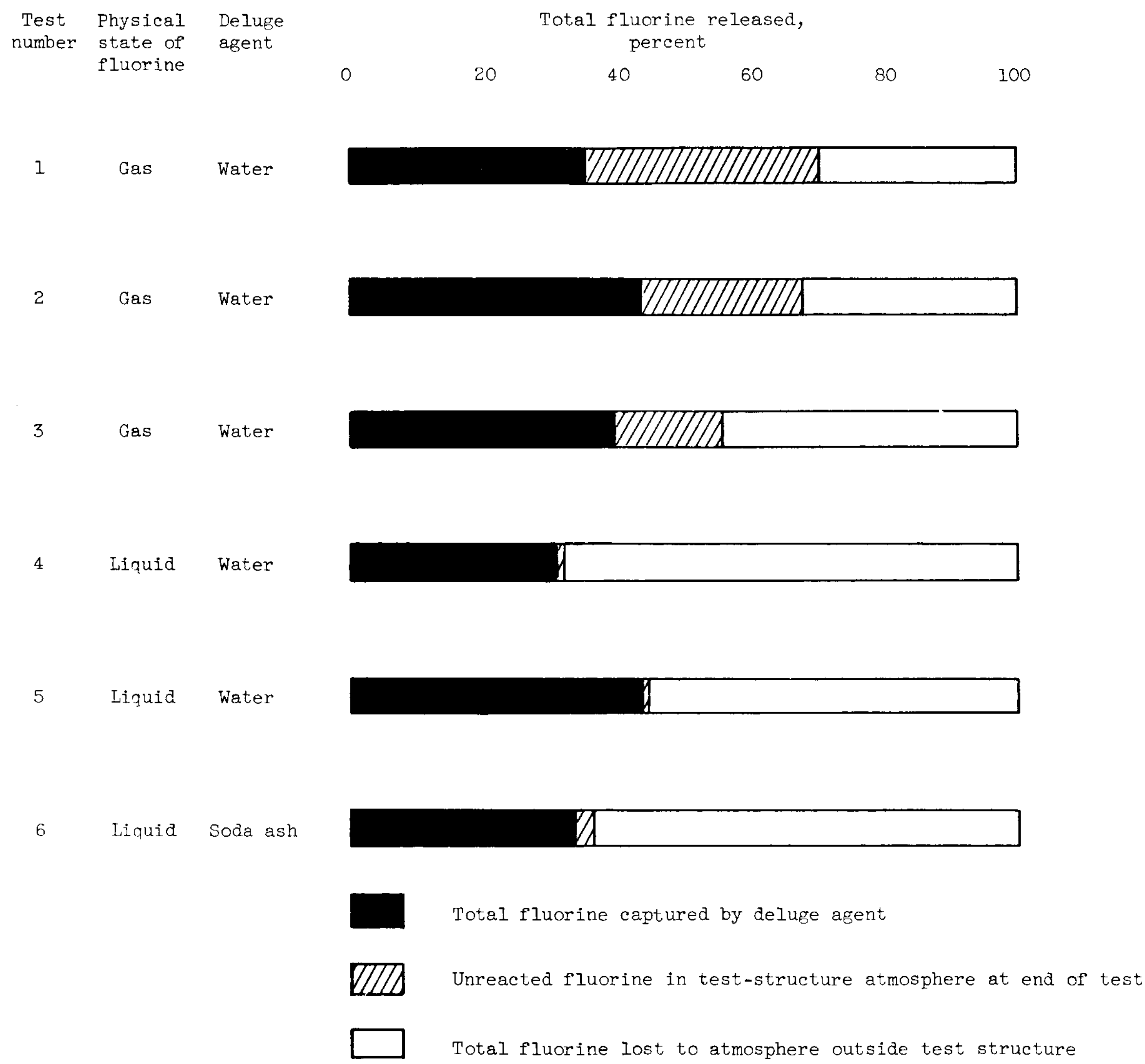


Figure 2. - Results of fluorine spill tests.